

Intercomparison INAA / PIXE for the elemental concentrations of zinc, iron and potassium in air particulate matter

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The awareness of environment degradation in a way that may influence health has increasingly been attested by several epidemiological and toxicological studies in many places of the globe, as well as in Portugal. Although the considerable progress achieved, during the last decades, in this field of science, many doubts still persist. In particular how air particulate matter originated from anthropogenic activities interact with the human systems is a question under debate. The association of the particulate matter with some lung diseases seems to be better defined if only fine particles are considered [1].

Since 1987 measurements of air particulate matter have been made in the Technological and Nuclear Institute using Instrumental Neutron Activation Analysis (INAA) [2] and Particle Induced X-ray Emission (PIXE) [3]. These techniques are complementary and have characteristics that make them highly suitable for conducting non-destructive multielement analysis of airborne particulate matter. Other methods usually require a time-consuming dissolution of filters and are generally only applicable to one, or a small group of elements [4]. The objective of this work is to compare the performance of INAA and PIXE in determining the elemental concentrations of zinc, iron and potassium in air particulate matter. In this work both PM_{2.5} (EAD < 2.5 µm) and coarse fraction (2.5 µm < EAD < 10 µm) are considered. EAD concerns Equivalent Aerodynamic Diameter.

The values shown are from an area in the neighbourhood of Lisbon. The northern part of Lisbon is a very industrialised and populated area. Several large industries are running there for many years, for processing glass, electricity (fuel burning), fertilizers and chemical products, and cement. Also the area has small industries related to food processing and metallurgical work. Two years ago an incinerator started to burn domestic urban waste (about 2,000 ton. /year). This work is associated with the monitoring studies of this structure. The air particulate matter collectors are situated: in Bobadela, working since 25th January 1999 and the whole year around, in S. João da Talha working since 7th March 1999 on autumn and winter, and Póvoa de Santa Iria working since 22nd March 1999 on spring and summer.

The air collection is made with Gent collectors, developed by the University of Gent in Belgium [5, 6]. This kind of collector is equipped with a stacked filter unit, which carries two Nuclepore® polycarbonate 47 mm filters. The filters of 8 and 0.4 µm pore sizes are used in each of two stages. The air is sampled at a rate of 17 l/min, allowing the collection of coarse particles with 2.5 µm < EAD < 10 µm in the first stage and PM_{2.5} in the second stage. The collectors work for 24 hours periods. The sampling is made twice a week: one weekend day and one midweek day [7, 8].

The filter loads are measured by gravimetry using a 0.1 µg sensitivity balance. For elemental analysis the filters are cut into three parts: one half is analysed by INAA

[9], one quarter is analysed by PIXE [10], and the other quarter is kept for eventual replicates. Some 45 elements are determined and a few are determined by both techniques, as for instance zinc, iron, and potassium.

The availability of air particulate matter reference materials is scarce and therefore accuracy evaluation is not an easy task. It was possible to test INAA accuracy for Zn, and Fe determination, by using home-prepared solution spotted filters and BCR CRM 128 (fly ash from pulverised coal) comprised in methylcellulose films simulating dust charged filters [11].

The BCR filters have certified values for Fe, Cu, Zn, and As, and indicative values for Cr. Four replicates were prepared, and after irradiation (1h irradiation time), each replicate was measured in 4 different hyperpure germanium detectors (FWHM~1.8 keV at 1,332 keV). The results are presented in Figure 1. The horizontal lines in the box denote the 25th, 50th, and 75th percentile values. The error bars denote the 5th and 95th percentile values. The two symbols below the 5th percentile error bar denote the 0th and 1st percentile values. The two symbols above the 95th percentile error bar denote the 99th and 100th percentiles. The square symbol in the box denotes the mean data.

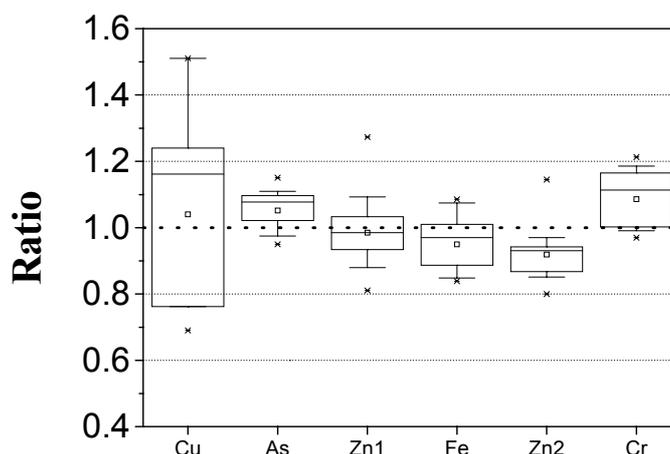


Fig. 1: Ratio (determined)/(certified or indicative value) for BCR128 reference material (Zn1 – determined via ^{69m}Zn ; Zn2 – determined via ^{65}Zn). Uncertainties of certified values for Cu, As, Zn, and Fe are lower than 5%; the uncertainty on Cr indicative value is larger than 5%.

Zinc determined via ^{65}Zn (1115 keV) is systematically lower than the certified value, being the mean of the ratios 0.92 and the ratio error 6%. For zinc via ^{69m}Zn (438 keV), the mean of the values is 0.98 and the ratio error is 30% (the counting statistic error varied between 5 and 17%). Nevertheless, it may be said that the results obtained via both nuclides are in good agreement with the certified values.

For Fe, the mean ratio is 0.94 and the ratio error is 5%. The contents determined in the filters were very often lower than the certified value, but again it may be said that there is a good agreement

For Cu, As, and Cr, there is also a good agreement with the certified values, with copper measurements reflecting the large statistics errors on peak areas.

Therefore, no systematic errors were observed and the agreement is better than 90%.

Standard solutions (AAS standardised solutions (1g/l)) of known amount of Na, K, Fe, Ba, Cd, Co, Zn, and Ca were spotted after dilution onto Nucleopore® polycarbonate filters, trying to simulate concentrations of the order of magnitude of the actual filters.

After spotting eight filters supported in glass material each, they were dried under an infrared lamp, irradiated for 11h, and measured each in the four detectors. Figure 2 shows the results. The signs have the same meaning as in Figure 1.

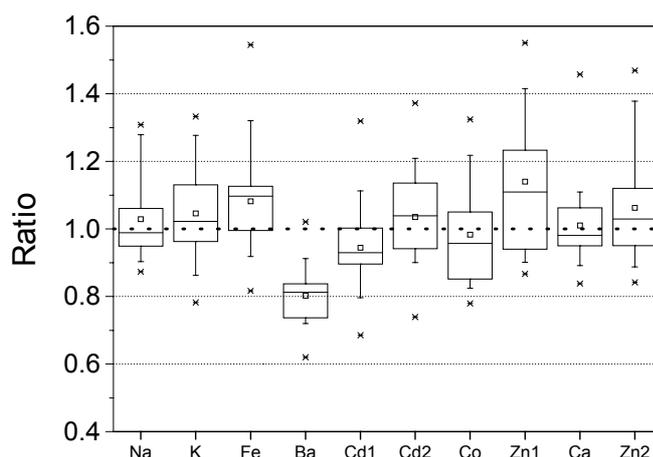


Fig. 2: Ratio (determined/expected value) for home-made filters. (Cd1 – determined via ^{115}Cd ; Cd2 – determined via $^{115\text{m}}\text{In}$; Zn1 – determined via $^{69\text{m}}\text{Zn}$; Zn2 – determined via ^{65}Zn). Uncertainties on the expected values are between 5 and 10%.

The agreement for K and Fe is quite good being the mean of the ratios 1.04 and 1.08, respectively (expected value is $5\mu\text{g}$). The ratio error for these elements is 6%.

Contents determined for Zn via $^{69\text{m}}\text{Zn}$ are very spread, and the expected value of $0.5\mu\text{g}$ was very often exceeded. The mean of the ratios for Zn via $^{69\text{m}}\text{Zn}$ is 1.13 and the ratio error 30%. Values for Zn via ^{65}Zn are less spread and the ratio is well distributed around 1; the mean of the ratios is 1.06 and the error associated 8%.

As to Na, Ba, Cd, Co, and Ca, the agreement is quite good except for Ba.

Therefore no systematic error was observed and the accuracy is better than 90% except for Ba and Zn via $^{69\text{m}}\text{Zn}$.

The results obtained for zinc by both INAA and PIXE in Bobadela, S. João da Talha and Póvoa de Santa Iria are compared (see Figures 3 and 4).

The two techniques compare better in the fine fraction than in the coarse one. This is expected since PIXE depends sharply of the sample homogeneity and we expect that fine fraction is more homogenised. For higher concentrations in fine fraction, the values tend to differ more, probably because PIXE is just analysing on surface and INAA analyses the total. Coarse fraction seems to be affected by a systematic error, since INAA values are mostly higher than PIXE results. Again this may reflect the surface characteristics of PIXE analysis.

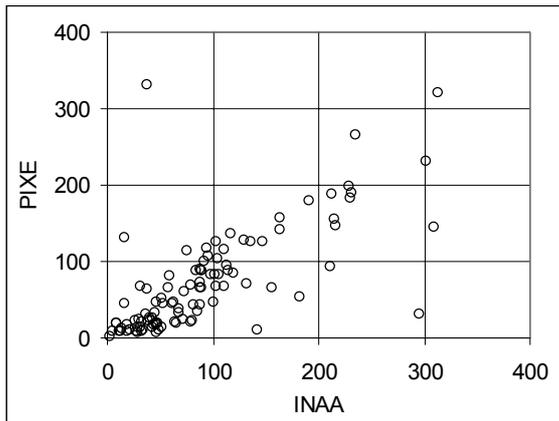


Fig. 3: Comparison INAA/PIXE for zinc in the fine fraction.

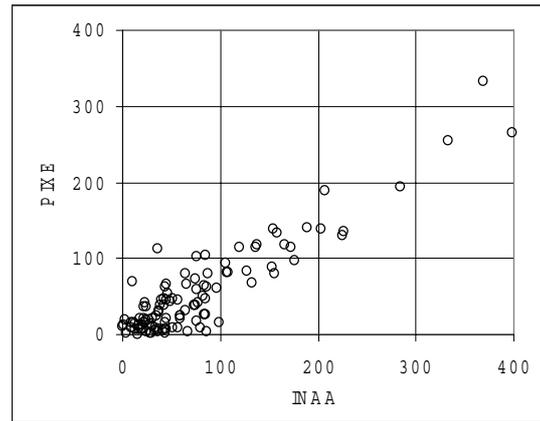


Fig. 4: Comparison INAA/PIXE for zinc in the coarse fraction.

Figures 5 and 6 show the comparison of Fe results in the fine and coarse fractions obtained by both INAA and PIXE.

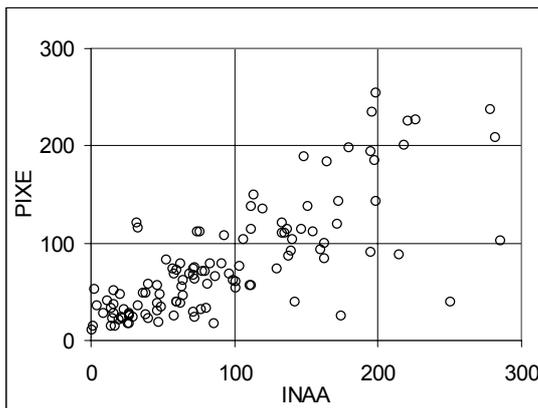


Fig. 5: Comparison INAA/PIXE for iron in the fine fraction.

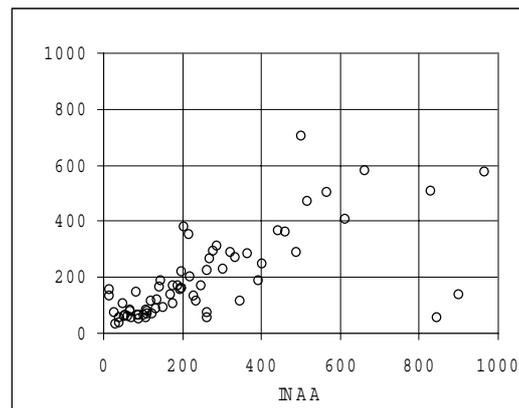


Fig. 6: Comparison INAA/PIXE for iron in the coarse fraction.

In fine fraction the situation is similar to the pointed out for Zn in fine fraction: larger differences are found when Fe concentrations increase. The coarse fraction is showing systematic errors only for higher concentration values.

Comparison between INAA and PIXE results for potassium in the fine and coarse fractions are shown in Figures 7 and 8.

The correlation in fine fraction is similar to zinc and potassium, quite good for lower concentrations and with larger differences on the high concentration levels. The coarse fraction does not show an evident systematic error, which might mean that K is superficially located in coarse air particulate matter.

In conclusion, accuracy of INAA in polycarbonate filter analysis is quite good. PIXE accuracy could not be ascertained due to the non-availability of adequate reference materials. Results obtained by INAA and PIXE in fine fraction compare quite well for lower concentration tending to present large differences for high concentrations.

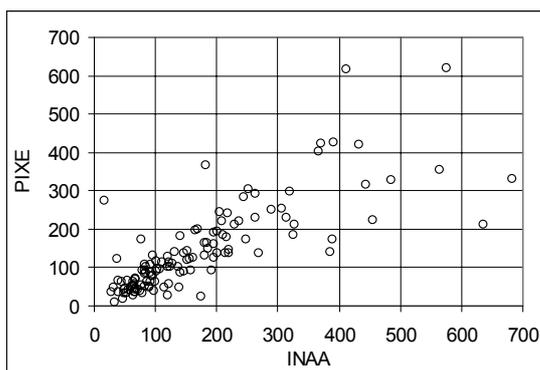


Figure 7: INAA and PIXE comparisons for Potassium in the fine fraction.

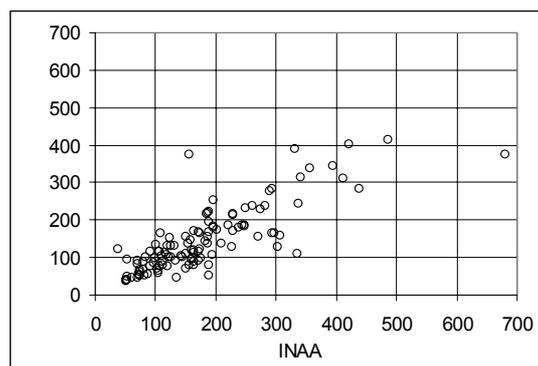


Figure 8: INAA and PIXE comparisons for Potassium in the coarse fraction.

Coarse fraction results are in worse agreement than the values obtained for the fine fraction, tending to present systematic errors, except for potassium. Heterogeneity and surface analysis were pointed out as causing the difference in analytical results. Also the particulate matter may not be homogenised through the whole filter and that may originate differences in the concentrations of the half filter analysed by INAA and the quarter analysed by PIXE. In general, it may be said that the techniques compare reasonably well.

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